

ISOCYANATE-FREE PRIMER COMPOSITION FOR GLASS AND GLASS CERAMICS

5 Technical Field

The invention relates to isocyanate-free primer compositions for glass and glass ceramics in order to improve the adhesion of an adhesive or a sealant.

10 State of the Art

Adhesives, coatings, sealants, floorings and other systems are based on the reactive binders. The adhesion of these reactive systems to diverse substrates is often unsatisfactory. Therefore, often the so-called "primers" are used. A primer
15 forms an adhesion bridge between the substrate and the used binder. A primer is also a chemically reactive system and is applied on the substrate.

In order to obtain a set-up of adhesion of the primer with the substrate, the primer must be provided with a definite time, the so-called "flash off time", in order to form
20 a film and at least to partially cross-link before the adhesive or any other reactive system can be applied. However, the application of this system is restricted during the so-called "open time" during which the adhesion to the primer is ensured. An adhesion to the primer is no longer ensured on exceeding the open time. Open time is thus determined in tests in which variably long period between
25 the application of the primer and the adhesive is maintained and the adhesion of the bonds after hardening of the adhesive is determined. As a model the adhesion between the primer and the adhesive or another reactive system is formed by a reaction between these materials. The ventilation time must be as

- short as possible in an industrial application in order to ensure a fast and cost-effective processing. This means that the adhesion set-up of the primer with the substrate must be as fast as possible so that an application of an adhesive or any other reactive system can be done as fast as possible. However, in doing this, the
- 5 problem of interruption in the production process occurs because of, for example, technical defects, end of shift or weekends, so that a longer period of a few hours to days or even weeks can elapse between the application of the primer and the application of the adhesive or any other reactive systems. This is especially disturbing in continuously running industrial applications. Moreover, the trend in
- 10 automotive engineering is to shift the pretreatment away from the industrial assembly line into the factory of the supplier so that an open time of up to a few weeks could elapse between the applications of the primer in the factory of the supplier to the application of the adhesive in the production factory.
- 15 There is a great demand for primers having long open times in order to also ensure a good adhesion in these cases.

Glass and glass ceramics are extremely important substrates for the bonding technology, particularly in automotive engineering. Traditionally, primers based on

20 isocyanates are used for this. On the one hand isocyanates are regularly the topic of controversial discussion concerning toxicity, and on the other hand, isocyanates are reactive substances. In particular, they react with the atmospheric humidity so that the number of free isocyanate groups is very considerably reduced within a short time after application of an isocyanate primer. Therefore, normal isocyanate-

25 based primers are generally suitable only for short open times.

US 4,963,614 describes a primer for glass which contains a silane and a polyisocyanate, a film-forming component as well as carbon black. However, the silane-polyisocyanate reaction product disclosed therein is not provided with an

isocyanate-reactive group, which infers to poor adhesion characteristics with polyurethane adhesive applied on it, particularly after cataplasma storage. No data is provided on the open time of these primers.

- 5 US 5,109,057 describes a primer which is produced from a polyurethane pre-polymer which is carrying isocyanate groups and a silane consisting of NCO-reactive functional groups. This primer seems to exhibit an improved UV-stability. No data is provided on the open time of these primers.
- 10 WO 02/059224 A1 describes a two-component primer, which comprises a curing agent comprising of an adduct of an alkoxy silane and a polyisocyanate having a mean NCO-functionality from 2.5 to 5.0 and an isocyanate content from 8 to 27 wgt.-%, and a lacquer resin reactive to the isocyanate groups as the second component. However no primary amino silanes are disclosed as alkoxy silane.

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With the state of art it is not possible so far to obtain an isocyanate-free primer which exhibits a good adhesion to glass and glass ceramics and a long open time.

Detailed Description of the Invention

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The task of the invention is to overcome the described disadvantages and problems of the primer for glass and make available a primer which also exhibits a good adhesion to glass and glass ceramics and a long open time. It was unexpectedly found that the disadvantages of the state of the art could be

25 eliminated by the inventive primer composition according to claim 1. At the same time a good adhesion at short flash off times, respectively at short waiting times between the application of the primer and the adhesive, is ensured.

Methods for Realization of the Invention

- The present invention relates to a primer composition comprising a compound **A1** which contains isocyanate-reactive groups. A polyisocyanate **A**, comprising at least three isocyanate groups, as well as at least one silane **B** of the formula (I), as well as a cross-linking agent **C** having three isocyanate-reactive functional groups are used for producing this compound **A1**.
- 10 Molecules which comprise formally two or more of the respective functional groups are designated in the entire document by the prefix "poly" in "polyisocyanate" and "polyol".
- By the term "isocyanate-reactive functional groups" those chemical functional groups which react with an aliphatic or aromatic isocyanate group at room temperature or at temperature of up to 100° C, if necessary in the presence of a suitable catalyst, are understood.
- 15 The polyisocyanate **A**, used for producing compound **A1**, has at least 3 isocyanate groups. In particular 3, 4, 5 or 6, preferably 3 or 4 isocyanate groups are present.
- 20 These polyisocyanates are preferably low-molecular polyisocyanates having a molecular weight of less than 2000 g/mol, particularly less than 1000 g/mol. The molecular weight preferably is between 400 and 900 g/mol.
- 25

On the one hand such low molecular polyisocyanates are the diisocyanate-polyol-adducts which are produced by the reaction of low molecular polyols with diisocyanates in excess of the diisocyanate leading to a NCO-functionality of three or more. Examples of such diisocyanate-polyol-adducts are those from a polyol,
5 as mentioned further below as cross-linking agent C, and an aliphatic or aromatic diisocyanate. In particular to be mentioned are adducts from trimethylolpropane, glycerol or pentaerythritol as polyol and HDI, TDI or IPDI as diisocyanate.

On the other hand, they are low molecular oligomers or polymers of diisocyanates.
10 For example it is here with polymeric MDI (4, 4'-diphenylmethandiisocyanate), such as for example the one which is commercially available as Voranate M-580 (Dow).

Particularly suitable are the low-molecular polymers of the monomers

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- HDI, for example commercially available as Desmodur N-3300 (Bayer), Desmodur N-3600 (Bayer), Luxate HT 2000 (Lyondell); or as Desmodur N-100 (Bayer), Luxate HDB 9000 (Lyondell);
- IPDI, for example commercially available as Desmodur Z 4470 (Bayer),
20 Vestanat T 1890/100 (Hüls), Luxate IT 1070 (Lyondell);
- TDI, for example commercially available as Desmodur IL (Bayer);
- TDI/HDI.

In particular, they are biuretes and isocyanurates, preferably of low molecular
25 diisocyanates. Diisocyanates particularly suitable for this are 2,4- and 2,6-toluylenediisocyanate (TDI), 4,4'-diphenylmethanediisocyanate (MDI) as well as its positional isomers, hexamethylenediisocyanate (HDI), 2,2,4- and 2,4,4-trimethyl-1,6-hexamethylenediisocyanate, tetramethoxybutane-1,4-diisocyanate, butane-1,4-diisocyanate, dicyclohexylmethanediisocyanate, cyclohexane-1,3- and 1,4-

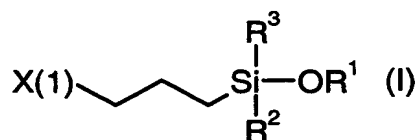
diisocyanate, 1,12-dodecamethylenediisocyanate, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (=isophorondiisocyanate or IPDI), as well as the hydrogenated compounds of the said aromatic compounds. Obviously, mixtures of diisocyanates are also possible for producing biuretes and isocyanurates.

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The polyisocyanate **A** is preferably an isocyanurate or a biuret of monomers selected from the group consisting of HDI, IPDI, TDI and mixtures thereof. It is especially an isocyanurate of HDI.

The silane **B** used for producing compound A1 has the formula (I).

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In formula (I) R^1 represents methyl or ethyl. Furthermore, R^2 represents a H, a C_1 -to C_4 -alkyl or OR^1 and R^3 represents a H, a C_1 -to C_4 -alkyl or OR^1 . X(1) denotes an isocyanate-reactive group or an organic residue carrying isocyanate-reactive groups and is a primary amino group or an organic residue which has at least a primary amino group. Preferably X(1) is NH_2 .

Preferably R^1 represents methyl. More preferred is $\text{R}^3 = \text{OR}^1$ and even more preferred is $\text{R}^3 = \text{R}^2 = \text{OR}^1$.

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Examples for suitable silanes **B** of the formula (I) are:

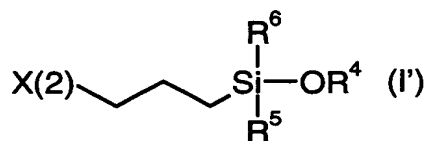
3-Aminopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, N-(2-aminoethyl)-3-aminopropyltriethoxysilane, 3-aminopropylmethyldimethoxysilane, 3-aminopropylmethyldiethoxysilane, 3-aminopropyldimethylmethoxysilane, 3-aminopropyldimethylethoxysilane, N-(2-

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aminoethyl)-3-aminopropylmethyldimethoxysilane, N-(2-aminoethyl-3-aminopropylmethyldiethoxysilane, N-aminoethyl-3-aminopropylmethyldimethoxysilane, N-aminoethyl-3-aminopropylmethyldimethoxysilane. 3-aminopropyltrimethoxysilane is preferred.

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In one embodiment of the invention in addition to the silane of the formula (I) at least another silane of the formula (I')



is used for producing compound **A1**.

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In formula (I') R^4 represents methyl or ethyl. R^5 also represents a H, a C_1 -to C_4 -alkyl or OR^4 and R^6 a H, a C_1 -to C_4 -alkyl or OR^4 . X(2) represents an isocyanate-reactive group or an organic residue carrying isocyanate-reactive groups and is a primary amino, mercapto or hydroxylic group or an organic residue which comprises at least one primary amino, mercapto or hydroxylic group. X(2) is preferably SH or NH_2 .

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Preferably R^4 represents methyl. $\text{R}^5 = \text{OR}^4$ is also preferred, more preferred is $\text{R}^6 = \text{R}^5 = \text{OR}^4$.

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Examples for suitable silanes **B** of the formula (I') are:

3-aminopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, N-(2-aminoethyl)-3-aminopropyltriethoxysilane, 3-aminopropylmethyldimethoxysilane, 3-aminopropylmethyldiethoxysilane,

3-aminopropyldimethylmethoxysilane, 3-aminopropyldimethylethoxysilane,
N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane, N-(2-aminoethyl)-3-
aminopropylmethyldiethoxysilane, N-aminoethyl-3-
aminopropylmethyldimethoxysilane, N-aminoethyl-3-
5 aminopropylmethyldiethoxysilane;

3-mercaptopropyltrimethoxysilane, 3-mercaptopropyltriethoxysilane, 3-
mercaptopropylmethyldimethoxysilane, mercaptopropylmethyldiethoxysilane.

10 3-Aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane or 3-
mercaptopropyltrimethoxysilane are preferred.

If several silanes are employed then these can be used as mixture or can be used
at different points in time during the production of **A1**.

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Particularly preferred are different silanes **B**. The two silanes, 3-
aminopropyltrimethoxysilane and 3-mercaptopropyltrimethoxysilane, are
preferably used for producing compound **A1**.

20 The cross-linking agent **C** used for producing compound **A1** has at least three
isocyanate-reactive groups. These isocyanate-reactive groups can all be identical
or independently different from one another. It is preferred that all groups are
identical. The isocyanate-reactive groups are especially selected from primary
amino group (NH₂), secondary amino group (NH), mercapto group (SH) or
25 hydroxyl group (OH). A mercapto or hydroxylic group is preferred.

At least three isocyanate groups are present, but can also be more, especially 3,
4, 5 or 6. 3 or 4 are preferred.

In case of the cross-linking agent **C** is preferably a polyol, particularly a triol.

5 The cross-linking agent **C** preferably has a molecular weight of 90 – 1000 g/mol, particularly 90 – 500g/mol, preferably 120 – 150 g/mol. It has advantageously an equivalence weight of 30 – 350 g/eq, particularly 30 – 170 g/eq, preferably 30 – 65 g/eq, related to the isocyanate-reactive functional group which in case of a polyol is the OH-equivalence weight.

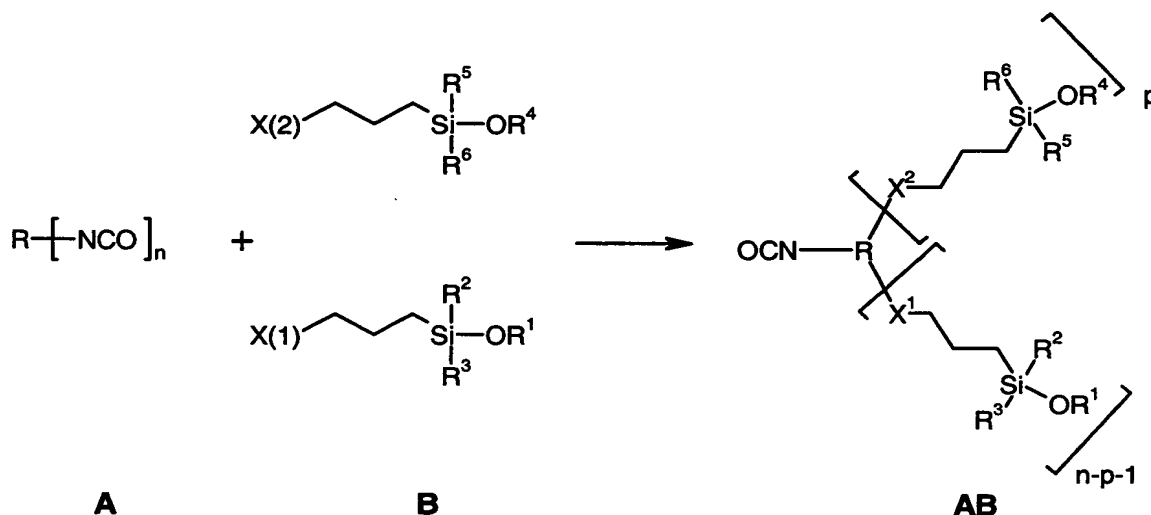
10 Higher molecular weights, respective equivalence weights, are less advantageous because this frequently leads to poor film properties, high viscosities or poor shelf life of the primer.

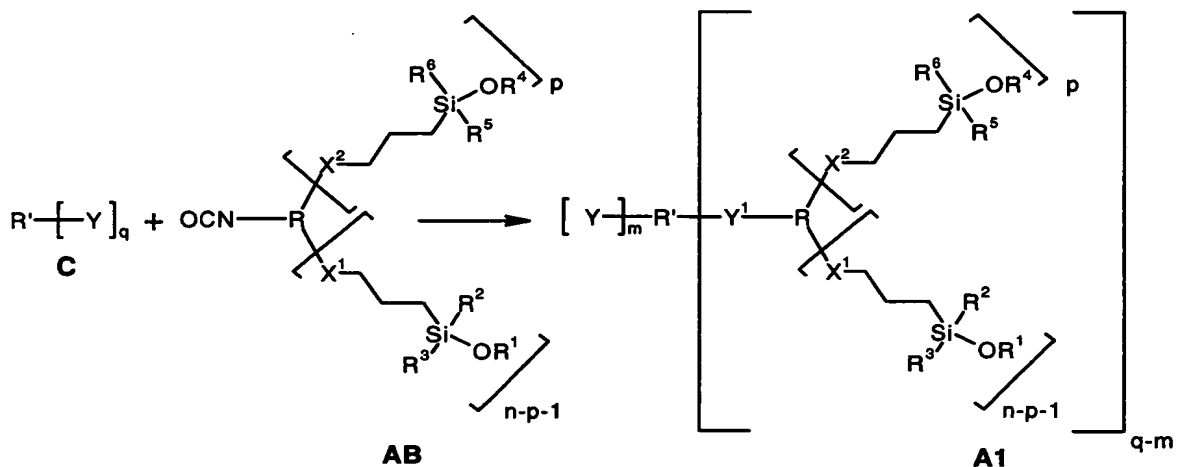
The cross-linking agent is, for example, pentaerythrite (=2,2-bis-hydroxymethyl-1,3-propanediol), dipentaerythrite (= 3-(3-hydroxy-2,2-bis hydroxymethyl-propoxy)-2,2-bis-hydroxymethyl-propane-1-ol), glycerol (= 1,2,3-propantriol), trimethylolpropane (= 2-ethyl-2-(hydroxymethyl)-1,3-propanediol), trimethylolethane. (= 2-(hydroxymethyl)-2-methyl-1,3-propanediol, di(trimethylolpropane) (= 3-(2,2-bis-hydroxymethyl-butoxy)-2-ethyl-2-hydroxymethyl-propane-1-ol), di(trimethylolethane) (=3(3-hydroxy-2-hydroxymethyl-2-methyl-propoxy)-2-hydroxymethyl-2-methyl-propane-1-ol), diglycerie (= bis-(2,3-dihydroxypropyl)-ether), triglycerine (= 1,3-bis-(2,3-dihydroxypropyl)-2-propanol; thioglycerine (=mercapto-1,2-propanediol), 2,3-dimercapto-1-propanol; triethanolamine (=tris-(2-hydroxyethyl)-amine) or
25 triisopropanolamine (=tris-(2-hydroxypropyl)-amine).

The cross-linking agent **C**, trimethylpropane, is particularly preferred.

The compound **A1** can be produced in different ways. In particular the compound **A1** can be obtained by the reaction of a cross-linking agent **C** with an intermediate product **AB** which is previously formed from a polyisocyanate **A** and at least one silane **B** of the formula (I) in a stoichiometric excess of the isocyanate groups of the polyisocyanate **A** in relation to the isocyanate-reactive groups of silane **B**.

Such a production method is illustrated, for better understanding, by means of the following reaction scheme simplified for a preferred case. However, this represents only an exemplary representation and cannot cover all the possible variants which can be produced particularly by different number of the reaction partners and stoichiometry.





Two molecules **B** are shown in this example. The application of different symbols for the residue shall illustrate that the residues can vary in the formula (I).

- 5 Therefore X(1) and X(2) correspond to the possible residues according to formulas (I) and (I').

R represents the polyisocyanate **A** after removal of all the isocyanate groups. Y represents an isocyanate-reactive group of the cross-linking agent **C** and R' the cross-linking agent **C** after removal of all the isocyanate-reactive groups. X¹, respectively X², respectively Y¹, represent the functional group which is produced from the reaction of X(1), respectively X(2), respectively Y, with isocyanate, i.e. particularly an urea, urethane or thiocarbamate group.

- 15 The indices n, respectively q, indicate the number of isocyanate groups of polyisocyanate **A**, respectively isocyanate-reactive groups of the cross-linking agent **C**, and correspond to the values already described for these.

Moreover, p, respectively n-p-1, indicate as to how many isocyanate groups of polyisocyanate **A** are bonded with silane **B** of variable type by forming the

intermediate product **AB**. The index p can assume values between 0 and $n-1$. One of the silanes **B** is merely bonded to the polyisocyanate **A** in the cases $p=0$ and $p=n-1$.

- 5 The intermediate product **AB** can comprise one or several non-reacted isocyanate groups. However, it is preferred that the intermediate product **AB** has only one free isocyanate group. Such a case is indicated in the above reaction scheme. If several free isocyanate groups remain in **AB**, as is the tendency, this leads to higher molecular species and thus to higher viscosities.

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Finally index m indicates as to how many free isocyanate-reactive functional groups the compound **A1** has. The index m particularly assumes the values 1, 2, 3, or 4, that is depending on q wherein $q - m \geq 2$. It is preferably 1 or 2. $m = 1$ is considered as particularly preferential.

15

The intermediate product **AB** can be produced by the participation of at least one silane **B**. But several silanes **B** can also participate, particularly 2 or 3. The intermediate product **AB** is preferably produced from two different silanes **B**. These two silanes of the formula (I) have different isocyanate-reactive groups $X(1)$ and $X(2)$.

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If several silanes **B** are used then these silanes can be directly used as mixture in the production or successively added. It appeared particularly suitable if at first one silane is added and a second or further silane is added to the reaction partner in a further step.

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The compound **A1** has at least one isocyanate-reactive functional group. Several such groups are possible. In particular it deals with 1, 2, 3 or 4 such groups,

preferably 1 or 2 such groups, particularly preferred 1 such group. The isocyanate-reactive group is particularly a primary amino group (NH₂), secondary amino group (NH), mercapto group (SH) or hydroxyl group (OH). Preferably it is a mercapto or hydroxylic group. If the compound **A1** has several such groups then
 5 these groups can all be same or different from one another.

On the one hand it is desirable that the compound is cross-linked by the cross-linking agent **C**. On the other it is desirable that not only the primer composition but also the compound **A1** no longer contains essentially any free isocyanate
 10 groups, i.e. they are essentially NCO-free.

Both can be controlled by the stoichiometric ratios in the reaction of the intermediate product **AB** with the cross-linking agent **C**. Therefore, it is particularly necessary that the isocyanate-reactive groups of the cross-linking
 15 agent are in the stoichiometric excess with regard to the isocyanate groups of the intermediate product **AB**. For this the relation r is defined as follows:

$$r = \frac{\text{Equivalent NCO-reactive groups (C)}}{\text{Equivalent NCO-reactive groups (A)} - \sum \text{Equivalent NCO-reactive groups (B)}}$$

20

The relation r amounts to the values of $> 100\%$. The upper limit represents that value at which formally a 1:1 adduct is formed between the cross-linking agent **C** and the intermediate product **AB**, i.e. in which the cross-linking agent no longer
 25 plays any cross-linking function. Therefore, the value of r should be clearly lower than this upper limit so that essential components of the cross-linked species are present. If too many 1:1 adduct molecules are present, then the stability of the primer is strikingly poor. The component of 1:1-adducts should not be more than

20% related to **A1**. Therefore the value of r has also a very high influence on the number of free isocyanate-reactive groups of the end-product **A1**.

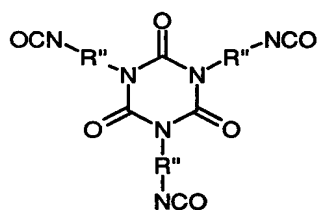
5 The person skilled in the art understands that, in addition to the compound **A1**, also such products in which free isocyanate-reactive groups are no longer present are formed on the one hand, as well as non-bridged reaction products, i.e. 1:1 adducts of the cross-linking agent **C** and intermediate product **AB**, are also formed on the other hand. However, it should be considered that the amount of these by-products is as little as possible.

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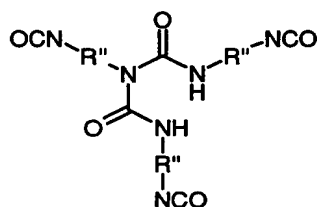
The values of r are between $> 100\%$ and $< 300\%$ for the specially preferred case in which the cross-linking agent **C** is a tri-functional molecule and the intermediate product **AB** contains one free NCO-group.

15 Here, the values of $105\% - 200\%$, preferably values of $105 - 150\%$, are to be particularly selected, to obtain a cataplasma-stable primer.

20 A specially preferred embodiment of the primer composition contains a compound **A1** which is produced from an isocyanurate of the formula (II) or a biuret of the formula (IIa), two silanes of the formula (III) and (IV), and trimethylolpropane (V).



(II)



(IIa)

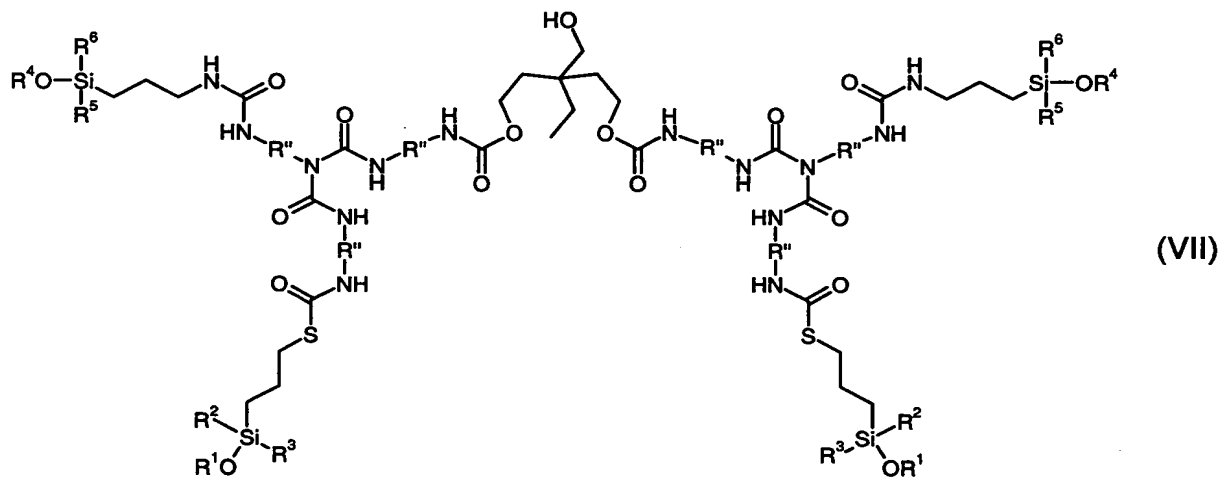
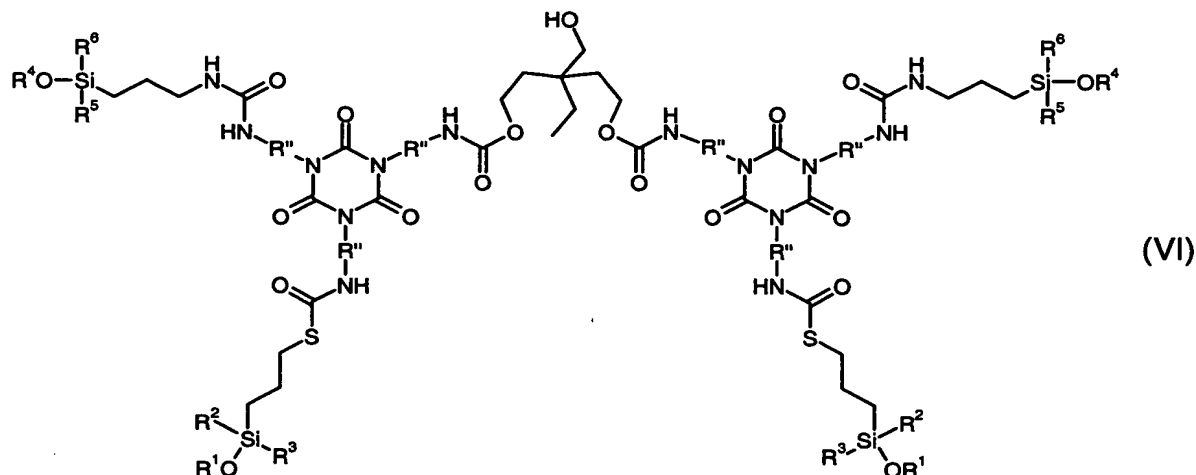


whereby the residues R^1 , R^2 , R^3 , R^4 , R^5 and R^6 represent the already defined residues. R'' is a divalent residue and particularly represents an aliphatic alkene residue, preferably the hexamethylene residue.

The intermediate product **AB** is preferably produced in a two-step process, particularly in which the mercaptosilane is used at first in a first step and the amino silane is used in a second step.

10

The compound **A1** thus produced may be represented by the formula (V) and formula (VII).



- 5 The compound **A1** has at least one isocyanate-reactive functional group. Several such groups are possible. It particularly deals with 1, 2, 3 or 4 such groups, preferably 1 or 2 such groups, particularly preferred 1 such group. The isocyanate-reactive group is preferably selected from a primary amino group (NH₂), secondary group (NH), mercapto group (SH) or hydroxyl group (OH). A
- 10 mercapto group (SH) or hydroxyl group (OH) is to be particularly preferred. If the

compound **A1** has several such groups then these groups can all be the same or different from one another.

The person skilled in the art understands that, in addition to the compound **A1**, also such products in which free isocyanate-reactive groups are no longer present are also formed on the one hand as well as non-bridged reaction products, i.e. 1:1 adducts of the cross-linking agent **C** and intermediate product **AB**, are also formed on the other hand. However, it should be considered that the amount of these by-products is as little as possible.

- 10 In an embodiment the primer composition also comprises at least one solvent **LM1** which is inert to isocyanates at room temperature. This solvent is used preferably already for producing of compound **A1**, respectively of the intermediate product **AB**. The solvent can get into the primer formulation, if necessary, only after the production of compound **A1**. The solvent is a volatile solvent and, in addition to the aromatic solvent like xylene, toluene, mesitylene, particularly comprises esters, specially acetates and ketones. The solvent is particularly selected from the group consisting of xylene, toluene, acetone, hexane, heptane, octane, methylethyl ketone, methylpropyl ketone, methylisopropyl ketone, methylbutyl ketone, dieethyl ketone, diisopropyl ketone, methylacetate, ethylacetate, propylacetate, butylacetate, methoxyethylacetate, methoxypropylacetate and 2-(2-methoxy-ethoxy)-ethylacetate. These solvents are preferably used in mixtures.

- Further solvents **LM2** can be added to the primer after producing compound **A1**. These solvents can also be reactive to isocyanates. They are preferably slightly volatile solvents having a boiling point of less than 100° C. Alcohols such as methanol, ethanol, propanol, isopropanol and sec. butanol are particularly suitable for this. Isopropanol is particularly suitable.

Solvents are mainly used for reduction of the viscosity as well as for optimization of the flash off behavior.

Moreover the primer composition may contain the coupling agent **HV**. Titanates, zirconates or silanes represent exemplarily such coupling agents. In particular they are preferably silicon-organic compounds. On the one hand the said silanes **B** as well as 3-glycidyloxypropyl-trialkoxo silanes, methacryloxypropyltrialkoxo silanes as well as vinyltrialkoxo silanes are the preferred silicon-organic compounds.

Trialkoxo silanes are particularly preferred. It appears that this additional coupling agent is advantageously a trialkoxo silane comprising a primary amino group, particularly a trimethoxy silane comprising a primary amino group, or a trialkoxo silane consisting of a vinyl group.

Moreover, the primer composition can also contain a catalyst **KAT**, particularly a tin-organic catalyst. These catalysts are normally polyurethane catalysts. The tin-organic catalyst is preferably selected from the group consisting of dibutyltindilaurate, dibutyltindichloride, tinthioester complexes, mono-n-butyltintrichloride, di-n-butyltin oxide, di-n-butyltindiacetate and dibutyltincarboxylate.

Moreover, the primer composition can contain of a filler **F**, like for example silica, talc, chalks and carbon blacks. A specially preferred filler is carbon black.

Moreover, commonly used additives in the primer chemistry can be used. Examples of unlimited type for this are UV- and heat stabilizers, flow-control agents, film formers, thixotroping agents as well as chemical and physical drying agents.

A specially preferred embodiment of a primer composition comprises, in addition to the compound **A1**, at least one solvent **LM1**, at least one coupling agent **HV**, a catalyst **KAT** as well as carbon black as filler **F**.

- 5 The described composition is produced and stored by exclusion of moisture.

The primer composition is suitable as primer for diverse substrates. It is particularly suitable for glass, glass ceramics, metals and alloys as well as for diverse plastics. The inventive primer composition is specially suited for glass and
10 glass ceramics, particularly those used in automotive engineering.

It can be advantageous to pre-treat the substrates before the application. Such pre-treatment methods include physical and/or chemical pre-treatment, for example polishing, sandblasting, brushing etc, or treatment with detergents,
15 solvents, coupling agents, solutions of coupling agents.

The primer is applied to a substrate by means of brush, felt, cloth or sponge. This application can be done manually or automatically, particularly by means of robots. Moreover, several layers of the primer composition can also be applied.
20

The primer composition is advantageously used as primer for adhesives, sealants, floorings, particularly for 1-component, moisture-curing polyurethane adhesives or sealants based on polyurethanes or polyurethane-silane-hybrides. Preferred application fields of these primers are areas where industrially prepared
25 components are also bonded. It deals particularly with applications where the primer is applied in the supplier's factory.

The inventive primer composition is characterized by an excellent adhesion on glass and glass ceramics which, even after drastic stresses, such as for example
30 by cataplasma test (7 days storage in 100% relative atmospheric humidity at 70 °

C) remain intact. Moreover, the primer is characterized by a long open time of more than a month. The fact that the inventive primer can be used already after a short flash off times of typically 30 seconds is also extraordinary.

5 Examples

<u>Raw materials</u>	<u>Reference source</u>
Methyl-ethylketone ("MEK")	Scheller, Thommen
4-Toluensulfonylisocyanate ("TI")	Bayer
Desmodur N100 ("N100") (NCO-content 22%)	Bayer
3-Aminopropyltrimethoxysilane (Silquest A-1110) ("Aminosilane")	Osi Crompton
N-Butyl-3-aminopropyltrimethoxysilane (Dynasilan A-1189) ("sec.Aminosilane")	Degussa-Hüls
3-Mercaptopropyltrimethoxysilane (Silquest A-189) ("Mercaptosilane")	Osi Crompton
Vinyltrimethoxysilane (Silquest A-171) ("Vinylsilane")	Osi Crompton
Trimethylolpropane	BASF
Dibutyltindilaurate	Rohm & Haas

Primer Compositions

Exemplary Production of a Primer Composition: *P-01*

- 10 161.8 g Desmodur N100 is reacted with 54.2 g mercapto silane in a preliminary step in 54 g 1:1-solvent mixture of xylene and methoxypropylacetate in inert atmosphere during 4 hours at increased temperature. The mercapto silane is added in a slow manner.

- In a subsequent step 64 g of amino silane is slowly dropped into the product of the first step in the presence of 5 g of drying agent as well as 649 g methylethyl ketone in inert atmosphere. After termination of this reaction 11.5 g trimethyl propane is slowly added by stirring at increased temperature till no NCO-content can be measured. At the end the additional constituents like catalyst and vinyl silane are also added.
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		<i>P-01</i>	<i>P-02</i>	<i>P-03</i>	<i>P-04</i>	<i>P-05</i>	<i>P-06</i>	<i>P-07</i>	<i>Ref.</i>
A	N100	16.18	16.18	16.18	16.18	16.18	16.18	16.18	16.18
B	Mercaptosilane	5.42	5.42	5.42	5.42	5.42	5.42	5.42	5.42
B	Aminosilane	6.40	6.40	6.40	4.00	8.00	6.40	6.40	6.40
C	Trimethylolpropane	1.15	1.05	1.30	1.75	0.75	1.15	2.63	
	Xylene/Methoxy-propylacetate (1/1)(w/w)	5.40	5.40	5.40	5.40	5.40	5.40	5.40	5.40
	Methylethylketon	64.92	65.02	64.77	66.72	63.72	64.42	62.94	65.57
	Drying agent	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
	DBTL	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
	Vinylsilane						0.50	0.50	0.50
	<i>r</i>	120%	109%	135%	112%	134%	120%	274%	0%

Table 1. Primer Compositions

		<i>P-01</i>	<i>P-08</i>	<i>Ref.</i>	<i>Ref-1.</i>	<i>Ref.-2</i>	<i>Ref.-3</i>
A	N100	16.18	16.18	16.18	16.18	16.18	16.18
B	Mercaptosilan	5.42		5.42	5.42		12.43
B	Aminosilane	6.40	11.35	6.40			
	sek.Aminosilane				8.40	14.90	
C	Trimethylolpropane	1.15	1.15		1.15	1.15	1.15
	Xylene/Methoxy-propylacetate (1/1)(w/w)	5.40	5.40	5.40	5.40	5.40	5.40
	Methylethylketon	64.92	65.02	65.57	65.02	65.02	65.02
	Drying agent	0.50	0.50	0.50	0.50	0.50	0.50
	DBTL	0.03	0.03	0.03	0.03	0.03	0.03
	Vinylsilane			0.50	0.50	0.50	0.50
	<i>r</i>	120%	120%	0%	120%	120%	120%

Table 1a. Primer Compositions (cont.)

The other examples ***P-02*** to ***P-08*** were prepared in similar manner with the amounts indicated in table 1.

5

The reference example ***Ref.*** shows no cross-linking agent **C**. The reference examples ***Ref-1***, or ***Ref-2***, correspond to the examples ***P-01***, or ***P-08***, whereby the primary aminosilane was substituted by the molar amount of a secondary aminosilane. The reference example ***Ref-3*** corresponds to the examples ***P-01*** whereby the primary aminosilane was substituted by the molar amount of the mercaptosilane, and thus contains no primary aminosilane.

10

Pretreatment of the Substrate and Application of the Primer

<u>Substrate</u>	<u>Source</u>
Float glass	Firm Rocholl, Schönbrunn, Germany
5 Glass with bismuth-based ceramic coating Cerdec 14259	Firm Rocholl, Schönbrunn, Germany

The substrates were cleaned by a mixture of isopropanol/water (1/1 w/w). The primer was applied after a waiting time of 5 min. The non-tin-side of the glass was
10 used for adhesion tests.

Application of the Adhesive and Test Methods

After a waiting time t specified in table 2 after the application of the primer a bead
15 of adhesive was applied onto said primer. The following moisture curing polyurethane- or silane-modified polyurethane adhesives which are commercially obtainable from Sika Schweiz AG are used:

	Sikaflex®-250 HMA-1	("HMA-1")
	Sikaflex®-250 DM-1	("DM-1")
20	Sikaflex®-250 DM-2	("DM-2")
	Sikaflex®-555	("SF-555")

The adhesive was tested after a curing period of 7 days in a climatized room ("KL") (23° C, 50% rel. atmospheric humidity) as well as after subsequent
25 cataplasma storage (CP) of 7 days at 70° C, 100% rel. atmospheric humidity.

The adhesion of the adhesive was tested by means of "bead test". For this, incision is made at the end just over the adhesive surface bonding surface. The

sectioned end of bead is held with round pliers and pulled from the substrate. This takes place by careful rolling of the bead on the tips of the pliers as well as by placing a cut section perpendicular to the direction of the bead till the blank substrate. The bead speed of peeling off of the bead is to be selected in such a manner that about every 3 seconds a cut section must be made. The test distance must correspond to at least 8 cm. The assessment is made based on the amount of adhesive remaining on the substrate after peeling off of the adhesive (cohesive failure). The assessment of the adhesion properties is done by evaluating the cohesive part on the adhesion surface:

- 10 1 = > 95% cohesive failure
- 2 = 75 - 95% cohesive failure
- 3 = 25 - 75% cohesive failure
- 4 = < 25% cohesive failure

- 15 It is indicated by adding "FH" that the adhesive shows a film adhesion on the primer leading to a fracture between the primer and adhesive. It is indicated by adding "P" that the primer peels off from the substrate and therefore the adhesion of the primer to the substrate represents a weak point. Test results with cohesive failures of less than 75% are considered as being unsatisfactory.

20

Results

- 25 Table 2 shows the results of the adhesion tests on glass of the examples ***P-01*** to ***P-07*** as well as the reference examples ***Ref.*** for short (1 minute, 10 minutes) and long (1 week, 2 weeks, 1 month) open times which represent the waiting times between the application of the primer and of the adhesive.

	Open time Storage	1 min		10 min		1 w		2 w		1 m	
		KL	CP	KL	CP	KL	CP	KL	CP	KL	CP
Primer	Adhesive										
P-01	HMA-1	1	1	1	1	1	1	1	1	4	1
P-01	DM-1	1	1	1	1	1	1	3FH	1	2	1
P-01	DM-2	1	1	1	1-2	1	1	1	1	1-2	1
P-01	SF-555	1	1	1	1-2	1	1	1	1	1	1
P-02	HMA-1	1	1	1	1	1	1	1	2	4	1
P-02	DM-1	1	1	1	1	1	1	1	2	2	1
P-02	DM-2	1	1	1	1	1	1	1	1	1-2	1
P-02	SF-555	1	1	1	2P	1	1	1	1	1	1
P-03	HMA-1	1	1	1	1	1	1	1	3	4	1
P-03	DM-1	1	1	1	1	1	1	1	1	2	1
P-03	DM-2	1	1	1	1	1	1	1	2	1-2	1
P-03	SF-555	1	1	1	1	1	1	1	1	1	1
P-04	HMA-1	1	1	1	1	1	1	2	2	4	1
P-04	DM-1	1	1	1	1	1	1	1	1	3	1
P-04	DM-2	1	2-3P	1	1	1	1	1	1	2-3	1
P-04	SF-555	1	1	1	1	1	1	1	1	1	1
P-05	HMA-1	1	2TB	1	1	1	1	1	4P	4	1
P-05	DM-1	1	1	1	1	1	1	1	4P	1-2	1
P-05	DM-2	4FH	4FH	1	4FH	1	1	1	4P	1-2	1
P-05	SF-555	2	3	1	1	1	1	1	1	1	1
P-06	HMA-1	1	2	1	4	2	1	2	1	4	1
P-06	DM-1	1	2	1	2	1	1	1	1	3	1
P-06	DM-2	1	2	1	4	1	2	1	1	1	1
P-06	SF-555	1	1	1	1	1	4	1	1	1	4
P-07	HMA-1	3	4	3	4	1	1	1	3-4	1	4
P-07	DM-1	3-4	3	3	4	1	1	1	2-3	1	1
P-07	DM-2	3	3	3	4	1	2	1	3-4	1	1
P-07	SF-555	1	1	1	1	1	1	1	3-4	1	3
Ref.	HMA-1	4	4	4	4	4	4	4	4	4	4
Ref.	DM-1	4	4	4	4	4	4	3	4	3	4
Ref.	DM-2	4	4	4	4	4	4	3	4	4	4
Ref.	SF-555	1	1	1	1	1	4	1	4	1	4
-	HMA-1	4	4	4	4	4	4	4	4	4	4
-	DM-1	4	4	4	4	4	4	4	4	4	4
-	DM-2	4	4	4	4	4	4	4	4	4	4
-	SF-555	1	2-3	1	2-3	1	2-3	1	2-3	1	2-3

Table 2 Adhesion results of primers having variable open times.

	Substrate	Glass		Glass Ceramics	
	Open time	10 min		10 min	
	Storage	KL	CP	KL	CP
Primer	Adhesive				
P-01	HMA-1	1	1	1	1
P-01	DM-1	1	1	1	1
P-01	DM-2	1	1-2	1	1
P-01	SF-555	1	1-2	1	1
P-02	HMA-1	1	1	1	1
P-02	DM-1	1	1	1	1
P-02	DM-2	1	1	1	1
P-02	SF-555	1	2P	1	1
P-03	HMA-1	1	1	1	1
P-03	DM-1	1	1	1	1
P-03	DM-2	1	1	1	1
P-03	SF-555	1	1	1	1
P-04	HMA-1	1	1	1	1
P-04	DM-1	1	1	1	1
P-04	DM-2	1	1	1	1
P-04	SF-555	1	1	1	1
P-05	HMA-1	1	1	1	1
P-05	DM-1	1	1	1	1
P-05	DM-2	1	4FH	4FH	4FH
P-05	SF-555	1	1	1	1
P-08	DM-1	1	1	1	2
P-08	DM-2	1	2	1	2
P-08	SF-555	1	2	2	1
Ref-1	DM-1	4	4	3	4
Ref-1	DM-2	5	4	2	3
Ref-1	SF-555	2	2	3	3
Ref-2	DM-1	4	5	4	3
Ref-2	DM-2	4	5	1	2
Ref-2	SF-555	2	2	3	1
Ref-3	DM-1	3	4	3	3
Ref-3	DM-2	4	4	4	4
Ref-3	SF-555	1	2	2	1
-	HMA-1	4	4	4	4
-	DM-1	4	4	4	4
-	DM-2	4	4	4	4
-	SF-555	1	2-3	1	4

Table 3 Adhesion on glass and glass ceramics

Table 2 shows that the inventive primer is characterized by an excellent adhesion to glass. Moreover, it can be seen that the example **P-06** exhibits considerably poorer adhesions as compared to comparison to the other examples **P-01** to **P-05**, particularly at short open times, but is still clearly better than the reference example **Ref.** as well as the example without the primer.

Table 3 shows the comparison between adhesion to glass and glass ceramics in which the inventive primer exhibits extremely good adhesion both to glass and also to glass ceramics. In case of the silane modified adhesive Sikaflex®-555, it is apparent that the adhesion is also retained not only in air-conditioned storage but also in cataplasma also in case of glass ceramics. In case of primer **P-05** the adhesive exhibits a certain weakness in adhesion with the result that a film adhesion occurs, but this means that the primer shows a good adhesion on the substrate.

A primer **P-01f** filled with 10% carbon black was produced on the basis of primer **P-01**. Its adhesion results after different long storage are shown in table 4. The primer was stored for period indicated in the table at the stated temperature and subsequently applied to glass as described. After the stated open time the adhesive was subsequently applied and tested after 7 days of curing, respectively after the subsequent cataplasma storage of 7 days.

P-01f		Open time	3 min		10 min		2 m		3 m		4 m	
Tempe- -rature	Du- -ration	Adhesive	KL	CP	KL	CP	KL	CP	KL	CP	KL	CP
23°C	1 m	HMA-1	1	1	1	1	1	1	1	1	4	3
		DM-1	1	1	1	1	1	1	1	1	1	1
		DM-2	1	3	1	2	1	1	1	1	1	1
23°C	9 m	HMA-1	1	4	n.b.	n.b.	1	1	4	4	n.b.	n.b.
		DM-1	1	1	n.b.	n.b.	1	1	4	4	n.b.	n.b.
		DM-2	1	1	n.b.	n.b.	3	4	1	1	1	1
23°C	12 m	HMA-1	n.b.	n.b.	3	1	1	1	1	3	n.b.	n.b.
		DM-1	n.b.	n.b.	3	1	1	5	1	1	n.b.	n.b.
		DM-2	n.b.	n.b.	1	1	1	1	1	1	n.b.	n.b.
50°C	1 m	HMA-1	1	1	1	1	3	1	3	2	4	1
		DM-1	1	1	1	1	3	1	1	1	3	1
		DM-2	1	1	1	1-2	2	1	2	1	2	1

Table 4. Adhesions as function of storage duration and open time of **P-01f**
(n.b. = not determined)

It is seen from the results of table 4 that the primer exhibits long storage stability and has long open times.

- 5 The results of the accelerated ageing, i.e. 1 month at 50° C, show that especially the adhesion deteriorates at longer open times.